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Testing of Gaseous Fuels and Other Gases

DETERMINATION OF SULPHUR COMPOUND CONTENT

Hydrogen Sulphide Content, Cadmium Acetate Method

DIN 51 855 Part 4

Prüfung von gasförmigen Brennstoffen und sonstigen Gasen; Bestimmung des Gehaltes an Schwefelverbindungen; Gehalt an Schwefelwasserstoff, Cadmiumacetat-Verfahren

1 Range of application

The cadmium acetate method can be used to quantitatively determine different concentrations of hydrogen sulphide (> 1.0 mg/m³) in all gaseous fuels and other gases.

General details on the range of application, purpose, terms and details of further investigation methods for determining the content of sulphur compounds in gaseous fuels and other gases are given in DIN 51 855 Part 1.

2 Other relevant Standards

DIN 1333 Part 2	Presentation of numerical data; rounding
DIN 12 380	Laboratory glassware; Erlenmeyer flasks, narrow-necked
DIN 12 385	Laboratory glassware; Erlenmeyer flasks, wide-necked
DIN 12 387	Laboratory glassware; Erlenmeyer flasks, with taper sleeve, taper 1 : 10
DIN 12 445	Laboratory instruments of glass; short-stem funnels
DIN 12 448	Laboratory equipment made from paper fibre materials; paper filters
DIN 12 596	Laboratory glassware; gas washing bottles; shape according to Drechsel
DIN 12 700 Part 3	Laboratory glassware; burettes with a lateral cock
DIN 51 848 Part 1	Testing of mineral oils; test errors; general, terms and their use in conditions of delivery
DIN 51 851	(Draft December 1978) Testing of gaseous fuels and other technical gases; calculating the reduced gas volume
DIN 51 853	Testing of fuel gases, protection gases and waste gases; sampling
DIN 51 855 Part 1	Testing of gaseous fuels and other gases; determination of sulphur compound content; range of application purpose, terms

3 Units

3.1 For gaseous fuels and other technical gases mg/m³ [1])

3.2 For liquid gases mg/kg or ppm

4 Brief description of the method

On passing a measured quantity of gas through a cadmium acetate solution, the hydrogen sulphide is converted quantitatively into difficultly soluble cadmium sulphide.

[1]) Gas concentrations in mg/m³ are based on the reduced gas volume (0 °C; 1.01325 bar, dry).

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The cadmium sulphite precipitate is subsequently decomposed with hydrochloric acid and the re-formed hydrogen sulphide is determined iodometrically.

These reactions take place according to the following equations:

$$H_2S + Cd(CH_3COO)_2 \rightarrow CdS + 2\ CH_3COOH$$
$$CdS + 2\ HCl \rightarrow H_2S + CdCl_2$$
$$H_2S + J_2 \rightarrow 2\ HJ + S$$
$$2\ Na_2S_2O_3 + J_2 \rightarrow 2\ NaJ + Na_2S_4O_6$$

5 Designation of the method

Test — DIN 51 855 - T 04 - 79

Designation

DIN main number

Part 4 of the Standard

Last two digits of the year of issue of the Standard

6 Equipment

6.1 Test apparatus

The test apparatus is constructed as a function of the gas pressure according to Fig. 1 or Fig. 2 and comprises:

2 DIN 12 596 - A 250 washing bottles with straight supply tube,

Gas meter, wet construction, with accessories (pressure meter, thermometer).

6.2 Cotton wool strainer for cleaning tarry and oily gases

.3 Condenser with receiver for investigation hot gases

6.4 Two DIN 12 700 SKA 50-01 burettes

6.5 Erlenmeyer flasks, DIN 12 380 - EE 250 flask or DIN 12 385 - WE 250 flask or DIN 12 387 - E 250 - ANS 29 flask or DIN 12 387 - E 250 - ANS 45 flask

6.6 Washbottle

6.7 DIN 12 445-100 funnel

6.8 DIN 12 448 - A110 - 2c circular filter

7 Chemicals

50 g of cadmium acetate solution $Cd(CH^3COO)^2 \cdot 2H^2O$, chemically pure, in 100 ml of glacial acetic acid and 850 ml of distilled water

Approx. 1 N acetic acid

.1 N or 0.01 N iodine solution

0.1 N or 0.01 N sodium thiosulphate solution

Starch solution: 1 g of starch, 25 g of sodium chloride NaCl, chemically pure, in 100 ml of distilled water

Hydrochloric acid, HCl, chemically pure, (density ρ = 1.19 g/ml)

8 Sampling

Sampling is carried out in accordance with DIN 51 853 by direct removal from the gas stream. During sampling and storage and up to the time of filtration, exposure to light must be avoided.

In the case of gases with a high hydrogen sulphide content, this can only be determined on random samples.

9 Procedure

Immediately before the test apparatus, tarry or oily gas is cleaned by a cotton wool strainer. When investigating hot gases, a condenser with receiver and a glass wool strainer are fitted before the test appartus. The feed line to the test apparatus must be made from glass or flint glass and must be as short as possible.

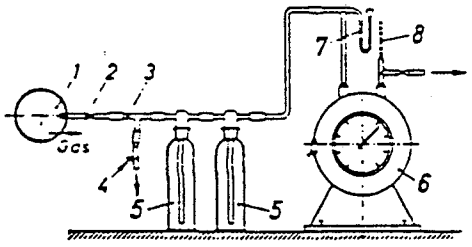

Figure 1. Test apparatus with adequate pressure

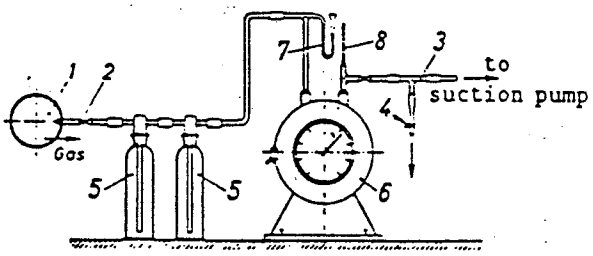

Figure 2. Test apparatus with inadequate pressure.

1	Gas line	5	Washing bottles
2	Sampling tube	6	Gas meter
3	T-piece	7	Pressure gauge
4	Screw-type pinchcock	8	Thermometer

The gas under investigation is passed through the darkened washing bottles (5) of the test apparatus, filled in each case with approximately 150 ml of cadmium acetate solution, until a clearly visible cadmium sulphide precipitate has formed in the first bottle. The solution in the second washing bottle must remain clear. The gas passage is regulated with the screw-type pinchcock (4) on the T-piece (3) in such a way that approximately 0.5 to 2 l/min flows through the test apparatus as a function of the H_2S content.

The gas stream which is passed through is measured with a gas meter. In order to calculate the reduced gas volume according to DIN 51 851*), the barometer reading is taken at least before and after the measurement, and during the determination pressure and temperature are measured on the gas meter.

The corresponding mean values are to be formed from the measured individual values. The relative humidity of the gas is assumed to be 100 % when using a wet gas meter ($\varphi = 1$).

The absorption solution is filtered when the gas has stopped flowing through. admium sulphide adhering to the walls of the washing bottles and to the supply tubes is washed onto the filter with approximately 1 N acetic acid. The precipitate is washed twice with the acetic acid and is introduced into the Erlenmeyer flask with the filter. After adding 150 ml of distilled water, a measured excess of 0.1 N iodine solution and 10 ml of hydrochloric acid, the glass stopper is immediately reinserted and the flask is agitated until the cadmium sulphide is completely dissolved. The unconsumed iodine excess is titrated back with 0.1 N sodium thiosulphate solution, whilst adding starch solution as the indicator.

If little cadmium sulphide is formed during the test, even when using a large quantity of gas (over 1000 litres) there is no need to filter the absorption liquid if other reducing substances are absent. In this case, after adding 0.1 N iodine solution, Hydrochloric acid and starch solution, the iodine consumption can be directly determined in the absorption solution.

When using a glass wool filter, the latter is rinsed out with distilled water at the end of the determination and the rinsing water is combined with the cadmium acetate solution.

f condensate is produced, the H_2S quantity in the condensate must also be determined and the result from the titration is to be added to the cadmium acetate solution.

An adequate quantity of cadmium acetate solution must be added to the condensate to determine the H_2S quantity. The cadmium sulphide formed is filtered off and treated in the same way as the cadmium sulphide obtained in the washing bottles.

If the expected consumption of titration solution is lower than 0.5 ml, 0.01 N solutions should be used.

10 Evaluation

10.1 If during sampling no condensate is separated, the hydrogen sulphide content can be calculated in mg/m^3 according to the equation (1)

$$\text{Hydrogen sulphide content} = \frac{1700 \cdot a}{V \cdot f_r} \qquad (1)$$

*) Subsequent edition at present still in draft form

10.2 If condensate is separated during sampling, the hydrogen sulphide content is to be calculated in mg/m³ according to the equation (2)

$$\text{Hydrogen sulphide content} = \frac{1700 \cdot a + 1000 \cdot G_K}{V \cdot f_r} \qquad (2)$$

Where:
V Measured gas volume in ℓ
f_r Reduction factor according to DIN 51 851*)
a 0.1 N iodine solution consumed, in mℓ
G_K Hydrogen sulphide quantity in the condensate, in mg

11 Statement of the result

If only a *single* determination is performed, the value obtained is to be given rounded as indicated below and referring to this Standard:

For a hydrogen sulphide content

- below 25 mg/m³ : 0.1 mg/m³
- from 25 to 500 mg/m³ : to 1 mg/m³
- over 500 mg/m³ : to 10 mg/m³.

If two individual determinations on the same sample are carried out (parallel determination) the difference between the two rounded individual values can be, for the hydrogen sulphide content:

- below 5 mg/m³ : to 0.5 mg/m³
- from 5 to 25 mg/m³ : to 1.0 mg/m³
- over 25 mg/m³ : to 4 % of the mean value of the two individual values.

This does not apply to individual determinations on samples not taken at the same time. The variations can be larger.

When rounding to the last decimal point to be given, account must be taken of DIN 1333 Part 2.

12 Testing errors

To evaluate the reliability of the results, the following features are used:

Repeatability
(one observer, one apparatus)

The difference between two test results obtained by the same observer with the same test material would in the long run only exceed the values given in the following Table in one out of 20 cases with normal and correct performance of the test method.

Hydrogen sulphide content mg/m³	Repeatability	
	absolute mg/m³	relative % of the numerical average value
below 5	0.5	-
5 up to 25	1	-
over 25	-	4

Further Standards

DIN 51 622 Liquefied petroleum gases; propane, propene, butane, butene and their mixtures; quality requirements

Explanations

This Standard was prepared by cooperation of the Working Committee NMP 622 "Requirements on and testing of fuel gases" as the Joint Committee of the Normenausschuss Bergbau (FABERG) (Standards Committee Mining Technology) and the Normenausschuss Materialprüfung (NMP) (Standards Committee Material Testing) as well as the Fachausschuss Mineralöl- und Brennstoffnormung (FAM) (Special Committee on Standardization of Mineral Oils and Fuels) of the NMP, and the Normenausschuss Gastechnik (NAGas) (Standards Committee Gas Technology).